X-Ray Diffraction and Melting-Point Data on Some Binary Mixtures of Trans-6 Through 12-Octadecenoic Acids and Their Dihydroxystearic Acids[1]

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X-RAY DIFFRACTION and melting-point data on the pure *trans*-6- through 12-octadecenoic acids and the corresponding dihydroxystearic acids have recently been reported (2-6). In this note we wish to describe the results of similar work on some binary mixtures of the *trans* acids and of the dihydroxystearic acids. This work was done as part of a program on the identification of compounds which are isolated from autoxidation, hydrogenation, and isomerization studies on long-chain compounds.

Experimental

Starting Materials. *Trans*-6-, 7-, 8-, and 11-octadecenoic aiids were prepared by the procedures of Fusari, Greenlee, and Brown (2). *Trans*-9-octadecenoic acid (elaidic acid) was prepared from oleic acid by isomerization with powdered selenium at 220° (8). The high-melting dihydroxystearic acids were prepared from these acids by hydroxylation with hydrogen peroxide in formic acid solution (2, 7). The low melting dihydroxystearic acids were similarly prepared from the *cis*-isomers.

X-Ray Technique. This has already been reported (9). In order to obtain the materials in a suitable crystalline state, the unsaturated acids were dissolved in acetone and the solutions were evaporated to dryness under a stream of nitrogen; ethanol was employed with the dihydroxystearic acids.

Melting Points. These were determined by the capillary method, employing samples which had been prepared for x-ray examination as described in the preceding paragraph. Within the melting range the temperature was raised at a rate not exceeding 0.25° per minute.

Results and Discussion

Table I summarizes the results obtained on the pure acids. The agreement between our results and the published ones are, in general, extremely good.

Table II summarizes the results obtained on 50:50 binary mixtures. All binary mixtures of *trans*-octadecenoic acids show marked depressions in melting point, but whether the melting range is narrow or wide depends on the components of the mixture. Mixtures of even-even (these refer to the number designating the position of the double bond) or odd-odd acids show marked depressions but narrow ranges (usually 1-1.5°) whereas mixtures of odd-even acids show broad melting ranges (usually 5-6°). The x-ray

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TABLE I

Melting Point and X-Ray Diffraction Data on Pure Acids

Trans-Octadecenoic Acid			High-Melting Dihydroxystearic Acid [a]			Low-Melting Dihydroxystearic Acid [b]		
	M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å
6-	52.7-53.4	44.9	6, 7-	122.8-123.3	45.2	6, 7-	114.0-115.0	45.4[3],44.4[5]
7-	43.7-44.1	49.0	7, 8-	132.7-133.0	41.8[c]	7, 8-	95.0- 96.0[4]	38.5[3]
8-	50.5-51.2	44.9	8, 9-	117.0-117.7	43.6	8, 9-	95.0- 95.6	45.6
9-	43.7-43.9	49.0	9,10-	130.7-131.0	41.8[c]	9,10-	94.7- 95.1	39.1
10-	52.0-52.6[4]	45.5[6]	10,11-	120.0-121.0[4]	43.9[5]	10,11-	98.0- 99.5[4]	45.5[5]
11-	43.5-44.1	49.0	11,12-	127.5-128.0	41.8[c]	11,12-	92.5- 93.0	39.0
12-	52.0-53.0[4]	45.5[6]	12,13-	119.0-120.0[4]	43.9[5]	12,13-	96.0- 97.0[4]	45.5[5]

[a] Prepared from *trans*-octadecenoic acids by hydroxylation with performic acid.
[b] Prepared from *cis*-octadecenoic acids by hydroxylation with performic acid.
[c] These have the same long-spacing but the intensities for a given order vary from compound to compound.

TABLE II

Melting Point and X-Ray Diffraction Data on 50:50 Binary Mixtures

Trans-Octadecenoic Acids			High-Melting Dihydroxystearic Acids			Low-Melting Dihydroxystearic Acids		
	M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å		M.P., °C.	Long Spacing Å
6-+ 8-	44.6-46.1	38.9[a]						
7-+ 9-	36.7-38.0	46.0[a]	7, 8-+ 9,10-	118.0-121.6	....[c]			
7-+11-	34.5-35.7		7, 8-+11,12-	117.0-122.0	....[c]			
9-+11-	36.6-37.7	46.0[a]	9,10-+11,12-	116.5-122.0		9,10-+11,12-	83- 85	45.6[d]
6-+ 7-	37.8-43.8		6, 7-+ 7, 8-	115.0-123.0	....[b]			
6-+ 9-	37.2-43.2	....[b]	6, 7-+ 9,10-	111.0-123.0	....[b]	6, 7-+ 9,10-	87-110	45.6[d]
7-+ 8-	37.2-42.8	....[b]	7, 9-+ 8, 9-	111.0-123.0	....[b]	6, 7-+11,12-	88-106	45.6[d]
8-+ 9-	36.2-41.2	....[b]	8, 9-+ 9,10-	110.0-122.5	....[b]	8, 9-+ 9,10-	79- 85	45.6[d]

[a] A one-phase system was obtained different from that of either pure component.
[b] The diffraction patterns were the combined pattern of the two pure compounds.
[c] Long spacings are equal to the identical values of the two components and intensities of the various orders appear to be a summation of the corresponding intensities of the pure components.
[d] These have the same long spacing but the intensities for a given order vary from mixture to mixture.

diffraction pattern offers a simple explanation for this. Mixtures of even-even or odd-odd acids form a one-phase system; mixtures of odd-even form a two-phase system and give diffraction patterns in which those of the pure components are superimposed.

Similar results are obtained in the melting points of the dihydroxystearic acids. Binary mixtures (50:50) of the dihydroxystearic acids from odd-odd or even-even octadecenoic acids have melting ranges from 2-5° whereas those from odd-even acids have melting ranges from 6-18°.

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